

A new generation of more pH stable reversed phases prepared by silanization of zirconized silica

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Abstract

To further extend our studies in the search for reversed phases with enhanced durability at high pH, zirconized silica has now been explored as an alternative support. The synthesis of the new stationary phases involves silanization of a zirconium-modified silica support with a C₁₈ trifunctional silane, followed by endcapping. The chromatographic properties of the C₁₈ phases based on zirconized silica are similar to their titanized silica counterparts. Accelerated high pH stability tests, using phosphate mobile phases and elevated temperature, have shown that the zirconized silica phases have promising advantages not only over similarly prepared non-metalized phases but also over titanized silica C₁₈ phases.

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1. Introduction

Since the earliest days of HPLC column technology, the development of different stationary phases to obtain better separation efficiency and selectivity has been a driving force. Spherical micrometer-sized silica, with appropriate surface area and narrow mesopore size distributions, is the most popular chromatographic support for preparation of reversed phases [1] because it is possible to obtain effective and reproducible separations over a wide range of operating conditions. However, silica has some drawbacks such as enhanced solubility in basic mobile phases and at higher temperatures. Both these conditions reduce the lifetime of the HPLC column [2]. In addition, the new trends in HPLC to speed up separation and productivity [3], such as high temperature HPLC and ultra high pressure liquid chromatography (UHPLC) [4] will keep pushing research forward to more stable phases since most conventional RP silica phases do not withstand these new, more demanding conditions.

It is well known that polymeric C₁₈ phases [5,6] provide better stability at high pH, compared to conventional monomeric phases. However, surface coverage as well the amount of residual silanols is less reproducible when compared to the silica

modified with monomeric silanes. Another possible weakness with the C₁₈ polymeric phases is that densely bonded polymer chains on the surface provoke slower mass transfer kinetics.

Other successful examples of stationary phases with extended high pH and temperature tolerances are the bidentate phases [7]. The silanization step uses bidentate reagents having two silicons bridged by –CH₂CH₂– or –CH₂CH₂CH₂– groups and also having an appropriate C₁₈ pendant group. The bidentate silane species on the modified surface protects the silica support from dissolution. Column stability is measurably improved when compared with C₁₈ phases based on monofunctional silane chemistry.

Hybrid phases, introduced in 2000, had the objective of having stationary phases with the same high efficiency and good pressure resistance as the pure silica-based phases, combined with the advantage of wider pH stability of polymeric phases [8]. The breakthrough in this technology was the production of spherical organic–inorganic silica particles, synthesized by the sol–gel process from a mixture of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS). As a result, some hydroxyls are replaced by a methyl group and the final silanol concentration is reduced when compared to sol–gel silicas prepared from pure TEOS. After silanization, the residual silanol concentration is even lower, providing excellent peak shapes for highly basic compounds in neutral mobile phases. Another consequence of the reduced number of residual silanols on the hybrid silica surface is improved hydrolytic stability in high pH mobile phases,

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since these unreacted silanols on the surface are the points at which silica dissolution starts [8].

More recently, a bidentate silane has been used for the production of hybrid particles [9]. By replacing MTEOS with bis(triethoxysilyl)ethane, where the $-\text{CH}_2\text{CH}_2-$ fragment is attached to two triethoxysilyl groups, hybrid particles containing ethylene-bridging groups on the surface are obtained. As a result of the hydrophobicity of the bidentate groups, these second generation hybrid phases, initially prepared for use in UHPLC [9], exhibit even better mechanical [10], thermal and hydrolytic stability [11] than the hybrid phases prepared with methyl substitution. On the other hand, the C_{18} surface coverage of both of these hybrid phases is lower when compared to traditional octadecyl silica phases.

Porous graphitic carbon also has some attractive properties [12] because it is not affected by physical or chemical degradation at high temperature regardless of the composition of the mobile phase. However, the modification of the surface is difficult and the resulting non-polar phases show less than ideal stability.

Phases based on metal oxides, such as titania and zirconia have also been investigated as these oxides have excellent high pH stability in comparison with silica [13]. One limitation in the early stage of this technology was the difficulty in synthesizing these inorganic oxide particles with appropriate particle size and shape as well as with surface areas adequate for use in HPLC. Another problem was the chemical modification or organofunctionalization. The first attempts to modify these oxides by conventional silanization procedures were not promising, due to lower surface coverages and loss of the bonded phase when in contact with basic mobile phases [14].

To overcome these problems, the use of polymers (polybutadiene, polystyrene) and carbon coatings proved successful for zirconia phases [13] while hydrosilylation is an alternative procedure for the modification of titania [15]. The enhanced Lewis acidity of the residual groups on the surface, pointed out as a potential disadvantage of these phases, can be easily manipulated by the addition of buffers, such as amines or carboxylic acids (Lewis bases) to the mobile phase. Recent data on stability have shown that these metal oxide stationary phases are well suited for use at temperatures above 100°C using pure water as the mobile phase [16].

In our research group, silicas modified with titanium alkoxides have also been explored as promising supports for the preparation of both chemically bonded phases [17] and polymer-coated phases [18]. The main objective of these modifications was to make the silica support less sensitive to dissolution at higher pH due to the presence of a protective layer of metal oxide, without sacrificing the many advantages of the porous silica structure.

Evidence for the success of this approach was first obtained in the 1980s by Stout and DeStefano [19], who prepared a “stabilized” phase for the separation of proteins in buffered mobile phases. These authors described the modification of the HPLC silica with an aqueous solution of zirconium oxychloride before silanization. The chemically bonded diol phase showed better stability for separations at pH 9. A decade later, Kirkland et al.

[20], showed that “type A” silica-based reversed phases, having metal contaminants in the silica matrix, were more stable in basic mobile phases than the purer “type B” silica-based reversed phases, showing that the approach of introducing a metal oxide structure on the silica surface has promise.

$\text{SiO}_2/\text{ZrO}_2$ as well as $\text{SiO}_2/\text{TiO}_2$ materials have been investigated by Chen and coworkers [21–23] for the preparation of octadecyl-bonded phases. However, a layer-by-layer technique was employed to attach zirconia nanoparticles on the silica surface. This involves the adsorption of a sodium dodecylsulfate surfactant, followed by deposition of a zirconia sol. The process is repeated several times, the surfactant is eventually burnt off by calcination and the $\text{SiO}_2/\text{ZrO}_2$ support is modified with octadecyltrichlorosilane to prepare the octadecyl-bonded phase. Nonetheless, their chromatographic efficiencies were quite low.

The present work, wherein stationary phases are prepared from a zirconized silica support with chemically bonded C_{18} groups, extends our studies in the search for reversed phases with enhanced durability at high pH.

2. Experimental

2.1. Solvents and chemicals

For the preparation of the phases, $5\ \mu\text{m}$ spherical Kromasil silica (Lot AT0235 from Akzo Nobel, Bohus, Sweden, having an average pore diameter of 10 nm, BET surface area of $310 \pm 5\ \text{m}^2\ \text{g}^{-1}$ and pore volume of $0.9\ \text{ml}\ \text{g}^{-1}$), zirconium butoxide (80% m/m in butanol, Aldrich), octadecyltrimethoxysilane (Aldrich), trimethylchlorosilane (TMCS, Aldrich), and hexamethyldisilazane (HMDS, Aldrich) were employed. Aniline, caffeine, *N,N*-dimethylaniline (*N,N*-DMA), phenol, triphenylene and uracil (all also obtained from Aldrich) were used as received, as test compounds. Triethylamine (Aldrich) was distilled before use.

Benzylamine, ethylbenzene, butylbenzene, pentylbenzene, *o*-terphenyl, potassium salts (KH_2PO_4 and K_2HPO_4), potassium hydroxide and phosphoric acid were obtained from Merck. ZrO_2 (Alfa Aesar, 99.7%) was used as a standard for the XRF analyses. Methanol (MeOH), tetrahydrofuran (THF), isopropanol, toluene and acetonitrile (ACN) were HPLC grade and were purchased from Tedia. Deionized water was from a Milli-Q water system from Millipore. The mobile phases for the HPLC separations were prepared volumetrically from individually measured amounts of each component and were filtered through a $0.22\ \mu\text{m}$ Nylon membrane filter and degassed prior to use.

The commercial phases evaluated were: C_{18} (Akzo Nobel, laboratory-packed into $60\ \text{mm} \times 3.9\ \text{mm}$ columns) and X-Terra RP-18 (Waters, acquired pre-packed into a $50\ \text{mm} \times 4.6\ \text{mm}$ column).

2.2. Synthesis of the C_{18} zirconized silica phase (SiZrC_{18})

Following a procedure similar to that for titanization [24], batches of 10 g of silica were activated at 100 – 110°C under reduced pressure (0.8 mbar) for 8 h. The activated silicas were

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